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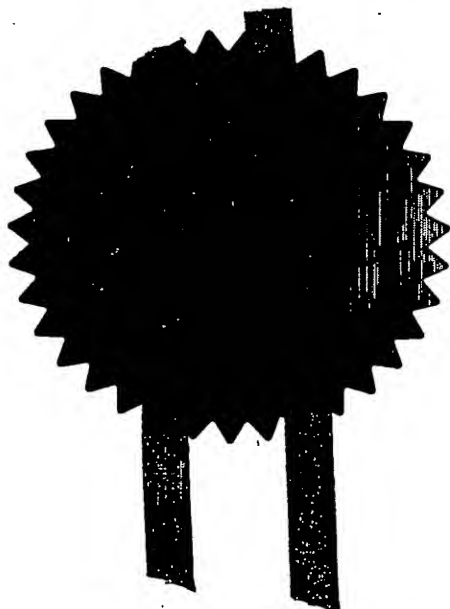
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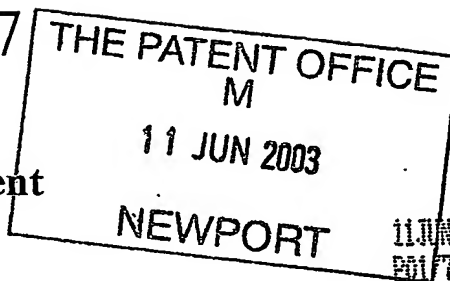
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23 June 2004

Patents Form 1/77

Request for grant of a patent

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1. Your Reference

BA/SLH/Y736

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08650509 001

4. Title of the invention

IMPROVEMENTS IN AND RELATING TO
URANIUM-CONTAINING MATERIALS

5. Name of agent

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Patents ADP number

190001

6. Priority claimed to:

Country

Application number

Date of filing

7. Divisional status claimed from:

Number of parent application

Date of filing

8. Is a statement of inventorship and
of right to grant a patent required in
support of this application?

YES

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

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Description

16 (x2) ✓

Claim(s)

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Abstract

Drawing(s)

1 (x2) ✓

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Priority documents

Translation of priority documents

Statement of inventorship and right to grant a patent (PF 7/77)

Request for a preliminary examination and search (PF 9/77)

Request for substantive examination (PF 10/77)

Any other documents (please specify)

11.

We request the grant of a patent on the basis of this application.

Signature

Date

APPLEYARD LEES

10 June 2003

Appleyard Lees

12. Contact

Ben Appleton – 0161 835 9655

IMPROVEMENTS IN AND RELATING TO URANIUM-CONTAINING
MATERIALS

Field of the Invention

5

This invention relates to methods of manufacturing uranium-doped material and material manufactured thereby.

Background to the Invention

10

The process whereby bulk X-Ba-Cu-O material (where X equals a rare earth element such as Yb, Nd, Sm, Ho etc) high temperature superconductor (HTS) are manufactured has been the subject of considerable scientific development over the last ten years. Large grain bulk X-Ba-Cu-O materials have significant potential for generating large magnetic fields, in excess of those achievable with conventional permanent magnets, for a variety of engineering applications such as magnetic bearings, MRI and flywheel energy storage applications. Recent work has focused on doping bulk X-Ba-Cu-O with uranium oxide per se, with the uranium in various valancy states, in order to enhance the flux pinning, and hence current carrying properties of large grain bulk superconducting materials. These materials may be fabricated by a variety of processes including melt processes to produce large single grain composites. Techniques of growing the superconducting crystals are described in Volume 1, Section B2.4.3.3 of "The Handbook of Superconducting Material" edited by Cardwell & Ginley, published by the Institute of Physics Publishing, UK.

30

In the various melt processes available, precursor powders of X-Ba-Cu-O and UO_2 are mixed either mechanically or by a solution based technique in a required stoichiometric ratios and compacted into the required geometry by uniaxial or hot cold isotatic pressing, for example. A small seed crystal of compatible crystallographic and chemical structure is usually placed on a surface of the powder compact (typically the upper surface) and the arrangement heated to the peritectically molten (i.e. partially molten) state. Alternatively, the seed crystal may be added to the compacted powders at an elevated temperature, either before or after peritectic decomposition. The sample and seed crystal is then cooled slowly through the peritectic solidification temperature during which process a single grain nucleates at the seed position and grows substantially outwards from the seed position. The decomposition and subsequent material growth processes produces uranium-doped X-Ba-Cu-O crystals. This material is fully superconducting and consists typically of a continuous superconducting microstructure (often referred to as the '123 phase) that contains discrete inclusions of a non-superconducting phase (often referred to as the '211 phase). The ability of these materials to generate or trap magnetic flux correlates either directly or indirectly with the size and distribution of the second phase inclusions. Doping uranium into the material has a significant effect on the refinement of existing inclusions and the generation of new second phase particle inclusions. Results have shown that uranium-doped second phase particle inclusions produced by co-melting of UO_2 and X-Ba-Cu-O material have the general formula X-Ba-Cu-U-O. It has been demonstrated

that the addition of uranium oxide per se has two key effects. These are:

- 5 a) the uranium acts as a refining agent or flux that produces a refined distribution of second phase inclusions with or without the presence of traditionally added platinum; the presence of uranium increases the achievable crystal growth rate; and
- 10 b) uranium forms a new secondary phase of particles having the formula $X_2Ba_6CuUO_y$ of sub-micron size throughout the crystal structure.

Although the inclusion of UO_2 particles produces
15 advantageous $X_2Ba_6CuUO_y$ particles, it is not possible using known techniques to predetermine size, number etc of the second phase particles within the crystal and the processing temperatures and times for manufacturing the crystal need to be carefully adjusted to ensure that
20 second phase particles are formed in sufficient numbers to be advantageous. Furthermore, using processes such as top-seed melt processing to produce the uranium-doped crystals by adding UO_2 , is relatively difficult and the conditions for processing need to be set within fairly
25 limited range in order for the UO_2 and X-Ba-Cu-O crystals to be able to tolerate the required temperatures and times in which to form second phase particles within the final crystal.

30 It would therefore be advantageous to provide a method of manufacturing a uranium-doped X-Ba-Cu-O type material in which the size and number of second phase particles can be predetermined before the crystal is formed. It would

furthermore be advantageous to provide a method which allows increased tolerance of the manufacturing conditions and parameters and which reduces processing temperatures and times to lower cost and increase optimisation of the crystal growth process.

It would furthermore be advantageous to produce a uranium-doped X-Ba-Cu-O crystal for which the first phase particles produces even stronger magnetic fields than in known uranium-doped crystals and in which addition of further dopants may increase overall performance of the crystal. It would also be advantageous to provide a uranium-doped X-Ba-Cu-O type material in which the addition of platinum, currently used to refine the particle size of doped X-Ba-Cu-O crystals, can be dispensed with without any detrimental effect to the properties of the crystals produced.

It is therefore an aim of preferred embodiments of the present invention to overcome or mitigate at least one problem of the prior art whether expressly disclosed herein or not.

Summary of the Invention

According to a first aspect of the invention there is provided a method of manufacturing a uranium-doped X-Ba-Cu-O material, the method comprising the steps of:

- a) mixing an X-Ba-U-O or X-Ba-Cu-U-O material with an X-Ba-Cu-O material; and
- b) crystallising the mixture;

wherein,

each X is independently selected from a rare earth (Group IIIB) element, yttrium, a combination of rare earth elements, or a combination of yttrium and a rare earth element.

By "X-Ba-Cu-O material", "X-Ba-Cu-U-O" material" and "X-Ba-U-O material" we mean compounds comprising said X, Ba, Cu, O and/or U elements whether only containing those elements or containing further elements as impurities or as part of said compounds.

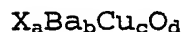
Suitably the X-Ba-Cu-U-O and X-Ba-U-O material comprise material of general formula:



wherein each X is as defined hereinabove; and wherein

w is 1 to 4; x is 1 to 6; y is 0 to 4; t is 0.3 to 2; and z is 3 to 20

Suitably the X-Ba-Cu-O material comprises material of the general formula



wherein each X is as defined hereinabove, and wherein

a is 1 to 4; b is 1 to 6; c is 0.5 to 4; d is 3 to 20.

Suitably each X is independently selected from one or more of yttrium, Nd, Sm, Ga, Eu or Ho, more preferably selected from one or both of yttrium and Nd, and most preferably each X is yttrium. Preferably each X is identical..

5

Preferably w is 1, 2 or 3; preferably x is 2 to 4; preferably y is 0.1 to 1 for X-Ba-Cu-U-O materials, more preferably 0.3 to 1; preferably t is 0.5 to 1, more preferably 1; and preferably z is 4 to 15, more preferably
10 5 to 12 and most preferably 6 to 8.

Preferably a is 1, 2 or 3; preferably b is 2 to 4; preferably c is 1 to 3, more preferably 1 or 3; preferably d is 4 to 15, more preferably 5 to 12 and most preferably
15 6 to 8.

Suitably the $X_aBa_bCu_cO_d$ is added in step a) to an amount of at least 50% w/w of the mixture, preferably at least 60% w/w, more preferably at least 70% w/w, still more
20 preferably at least 80% w/w, and most preferably at least 90% w/w of the total weight of the mixture. In particularly preferred embodiments the $X_aBa_bCu_cO_d$ is added in an amount of at least 95% w/w, and especially at least 99% w/w.

25

In contrast suitably the $X_wBa_xCu_yU_tO_z$ is added in step a) to an amount of at least 0.01% w/w, preferably at least 0.05% w/w and more preferably at least 0.1% w/w of the total weight of the mixture produced in step a).

30

Suitably the $X_wBa_xCu_yU_tO_z$ is a solid, and preferably a powder or granules.

The $X_aBa_bCu_cO_d$ may be any suitable physical state, which state may depend on the manner of crystallisation desired in step (b).

- 5 The $X_aBa_bCu_cO_d$ may be in molten or liquid form, and/or the method comprises a step prior to step (a) of substantially melting the $X_aBa_bCu_cO_d$. Alternatively the $X_aBa_bCu_cO_d$ may be in solid form, preferably in powder or granules form. Preferably the grain size of the powder or granules is at
 10 least 1 micron, and preferably the maximum grain size of the powder or granules is no more than 105 microns, more preferably no more than 75 microns.

Suitably step (b) comprises single crystal
 15 crystallisation.

Preferably step (b) comprises crystallisation of a mixture of $X_wBa_xCu_yU_zO_z$ in molten $X_aBa_bCu_cO_d$.

- 20 Crystallisation in step (b) may be effected by any suitable method.

Suitable methods of growing (crystallising) single crystals including sintering, grain growth, flux growth, top-seeded
 25 growth, solution crystallisation, floating zone crystallisation, travelling solvent crystallisation, electrocrystallisation and hydrothermal growth. Each of these techniques is described in detail in Volume 1, Section B2.4.3.3 pages 354-359 of the "Handbook of
 30 Superconducting Materials", published by the United Kingdom Institute of Physics, edited by Cardwell & Ginley, the contents of which is incorporated herein by reference.

Preferably step (b) comprises providing in a receptacle a mixture of $X_aBa_bCu_cO_d$ and $X_wBa_xCu_yU_tO_z$; melting the mixture; providing a seed or key to the receptacle; and
 5 subsequently manipulating the temperature of, or in the region of, the seed or key, to induce crystallisation of the molten mixture.

Preferably powders of $X_aBa_bCu_cO_d$ and $X_wBa_xCu_yU_tO_z$ are
 10 mechanically mixed or mixed using a solution based technique, in the required stoichiometric ratio, and then suitably compacted into the required geometry, by for example, hot or cold isostatic pressing.

15 The $X_aBa_bCu_cO_d$ and $X_wBa_xCu_yU_tO_z$ may be added to the receptacle in solid form and the mixture melted. Alternatively the $X_aBa_bCu_cO_d$ may be melted in the receptacle and solid $X_wBa_xCu_yU_tO_z$ added to the molten material.

20 The seed or key may be added to the molten mixture or added prior to melting the mixture. Preferably the seed or key is added to powdered $X_aBa_bCu_cO_d$ and $X_wBa_xCu_yU_tO_z$ and the powdered mixture subsequently melted.

25 The seed or key is preferably a crystal of compatible crystallographic and chemical structure to the $X_aBa_bCu_cO_d$.

Suitable seed crystals include the same $X_aBa_bCu_cO_d$
 30 material, and $X_aBa_bCu_cO_d$ material with a different X atom to the $X_aBa_bCu_cO_d$ material being crystallised, for example.

More preferably step (b) comprises top-seeded solution growth crystallisation (TSSG crystallisation), wherein $X_a\text{Ba}_b\text{Cu}_c\text{O}_d$ is melted to the required temperature, powdered $X_w\text{Ba}_x\text{Cu}_y\text{U}_t\text{O}_z$ is added to the molten mixture and a seed crystal arranged enter the molten mixture on a support member, the support member effecting the required temperature gradient to induce crystallisation around the seed crystal.

Suitably the mixture is melted to a peritectically molten state (i.e. partially molten state). Preferably the mixture of $X_a\text{Ba}_b\text{Cu}_c\text{O}_d$ and $X_w\text{Ba}_x\text{Cu}_y\text{U}_t\text{O}_z$ is heated to at least 900°C , more preferably at least 950°C and most preferably at least 1000°C , in order to melt the mixture into the preferably, peritectically molten state (partially molten state). Suitably the mixture is heated to no more than 1200°C , preferably no more than 1150°C and more preferably no more than 1100°C to melt the mixture to the peritectically molten state (partially molten state).

Manipulation of the temperature is preferably effected by cooling the seed or key, or the region around the seed or key at a rate suitable to induce peritectic solidification of the mixture. Suitably cooling is effected at a rate of no more than 6°C per hour, preferably no more than 5°C per hour. Suitably cooling is effected at a rate of at least 0.05°C per hour, preferably at least 0.075°C per hour and more preferably at least 0.1°C per hour.

The crystal growth may be effected under uniform thermal conditions, such as uniform temperature of the molten mixture, or may be effected under thermal gradient, in order to control the crystal growth rate.

The mixture maybe heated under air, oxygen-rich, or oxygen-depleted atmospheres in order to induce decomposition to the peritectically molten state.

5

The resultant uranium-doped X-Ba-Cu-O (XBCO) crystal is then preferably annealed at between 400°C and 700°C, more preferably in an oxygen-rich atmosphere, preferably for between 100 and 300 hours, more preferably for substantially 200 hours. The annealing step enables transformation of the crystal to the superconducting state.

The resultant superconducting material is believed to consist of a continuous superconducting microstructure (often referred to as the "123" phase due to a XBa_2Cu_3 - structure) that contains discrete inclusions of a non-superconducting phase (often referred to as the "211" phase due to a X_2BaCu - structure), and a second phase of X-Ba-Cu-U-O particle inclusions. The ability of this resultant material is to generate, or trap, magnetic flux correlates directly or indirectly to the exact size and distribution of the second phase inclusions of the 123 matrix. The method of uranium-doping described for the first aspect of the invention has a significant effect in the refinement of existing inclusions, and the generation of new second phase inclusions, to produce a superconducting material with properties superior to those displayed by similar materials manufactured by known prior art uranium-doping processes.

It has been found that the effect of adding $\text{X}_w\text{Ba}_x\text{Cu}_y\text{U}_t\text{O}_z$ particles to $\text{X}_a\text{Ba}_b\text{Cu}_c\text{O}_d$ provides (1) that the size and

number of uranium-containing particles can be pre-determined for the resultant crystal, before the crystal is formed; (2) superior refinement of the inclusions within the resultant crystal is effected to effect stronger magnetic fields within the structure, compared to crystals produced by known uranium-doping processes; (3) that the top seed processing procedure is simplified and accelerated compared to known processes; and (4) temperature of the crystal growing process can be optimised, and pre-planned, leading to superior quality, and superior effect, crystals.

The method may comprise mixing Y_2O_3 with the mixture produced in step a). The method may comprise adding Pt to the mixture produced in step a), but is not necessary due to the enhanced properties of the material produced by the method of the invention.

According to a second aspect of the invention there is provided a uranium-doped material manufactured by the method of the first aspect of the invention.

Brief Description of the Drawings

For a better understanding of the various aspects of the invention and to show how embodiments of the same may be put into effect, the invention will now be described by way of the accompanying Figure 1 which illustrates a front sectional view of a top-seed melt apparatus, in which a single crystal of uranium-doped X-Ba-Cu-O can be crystallised, which apparatus is described in detail in Journal of Material Science Letters, 14, p 1444 (1995).

Description of the Preferred Embodiment

We refer firstly to Figure 1.

5 A top-seed melt apparatus 2 consists of a pedestal 4 on which is mounted a furnace chamber 3, connected to heating means which enable heating to be effected within the furnace 3. Within the furnace chamber 3 is a seed holder arm 6 arranged to be located such that its distal end can
10 be positioned within a melt receptacle 10 located on the pedestal 4. At the distal free end of the free arm is a seed crystal 12 which is arranged to be lowered into the melt receptacle 10 in use. The apparatus in Figure 1 shows a growing crystal 14 connected to the seed crystal
15 12, growing in a melt solution present within the melt receptacle 10. The seed holder arm 6 is rotatable, and is such that rotation may be effected during growth of the crystal 14, in use. The airspace within the furnace 3 is a controlled atmosphere, in which the heat within the
20 furnace may be adjusted as desired. The seed arm 6 is also movable upwardly and downwardly with respect of the pedestal 4, such that during growth of the crystal 14, the seed arm may be retracted slowly from the melt receptacle 10, in order that further growth of the seed 14 may be
25 effected and a continual temperature gradient of the seed 12 and seed 14 effected in order to enable continued growth of the crystal 14.

30 In alternative embodiments of the apparatus 2, a cold finger may or may not be used to control grain nucleation and growth in the apparatus 2. Additionally, the seed crystal may be placed on an exposed surface of the

precursor pellet compact at room temperature, rather than at elevated temperature after melting or partial melting.

Example 1

5

An X-Ba-Cu-U-O material having a formula $\text{Y}_2\text{Ba}_4\text{Cu}_{0.7}\text{U}_{0.3}\text{O}_z$ (hereinafter "DU") was synthesised by conventional techniques. Particles of Y_2BaCuO_5 (Y-211) were synthesised along with particles of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y-123 particles), by a conventional solid state reaction technique.

The Y-123, Y-211 and DU powdered particles were, pressed into a compact pellet placed in the melt receptacle 10, and placed on the pedestal 4 of the top-seed melt apparatus 2 shown in Figure 1. The Y-123, Y-211 and DU particles were in the following proportions: Y-123 70 mol%, Y-211 30 mol% and 0.5% w/w DU.

The powder constituents in the melt receptacle 10 were heated to a temperature of 1000°C , in order to melt the powdered mixture into a peritectically molten state.

A seed crystal was connected to the melt arm 6 of the top-seed melt apparatus 2. The internal airspace of the furnace 3 was kept at 1000°C in order to heat the seed crystal to the same temperature as the melted constituents in the melt receptacle 10. The seed arm 6 was then lowered such that the seed crystal 12 just entered the molten mixture within the melt receptacle 8. The seed was then cooled at a rate of 0.01 to 1°C per hour in order to effect crystallisation of the melt 10 in the melt receptacle 8. As the seed 12 was cooled, the seed arm was

rotated such that the crystal 14 formed from the melt 10 across the entire distal surface of the seed 12. Also during crystallisation the seed arm was gradually retracted such that the emerging crystal 14 was always kept with only a single surface and region around said surface in contact with the melt 10.

Upon complete crystallisation, the single crystal produced was then subjected to an oxygen rich atmosphere at a temperature of between 500 and 700°C for 200 hours in order to anneal the crystal to enable transformation of the crystal to the superconducting state. The resultant superconducting material was shown to consist of a superconducting first phase microstructure of a Y-123 phase with contained discrete inclusions of a non-superconducting Y-211 phase and a second phase of DU-containing particles. The ability of the resultant crystal to generate, or maintain magnetic flux was found to be excellent, and greater than that of a traditionally manufactured uranium-doped superconducting XBCO crystal in which uranium dioxide is added to a melt of XBCO material. It is believed that the method of uranium-doping used in this example and this invention has a significant effect in refinement of existing Y-211 inclusions in the emerging superconducting crystal 14, to produce a superconducting material with properties superior to those displayed by similar materials manufactured by known prior art uranium-doping processes.

In particular, it was found that the resultant crystal provides the effect of strong magnetic fields within the doped structure compared to crystals produced by known uranium-doping processes and the top-seed processing

procedure enabled a highly efficient and accelerated process including temperature optimisation, which led to superior quality and superior effect crystals.

5 Example 2

The method of Example 1 was repeated but with a powdered mixture of 70% Y123, 20 mol% Y-211, 10 mol% Y_2O_3 and 0.5% w/w DU. The resultant crystal was found to achieve
10 even further improved overall performance such as stronger magnetic fields, and the enablement of partial or partial oxygenation of the material during the growing stage, as compared with Example 1.

15 In both the examples described above, it was found possible to dispense addition of platinum, generally used in the production of XBCO, uranium-doped superconducting crystals, without any detrimental effect to the properties of the crystals produced.

20

In further experiments, the DU component was replaced with uranium containing particles having the following formulas - $Y_3Ba_5U_2O_{15}$, $Y_3Ba_5U_2O_y$, $Y_3Ba_5UO_y$, $Y_3Ba_6U_2O_y$, $Y_2Ba_4UO_y$ and $Y_3Ba_6UO_y$, wherein y was 5 to 15.

25

Uranium-doped superconducting crystals produced by the method of Example 1 with the above mentioned further uranium containing compounds were synthesised and tested, and each was found to exhibit the same excellent magnetic
30 flux properties of the crystals produced in Example 1 and 2.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

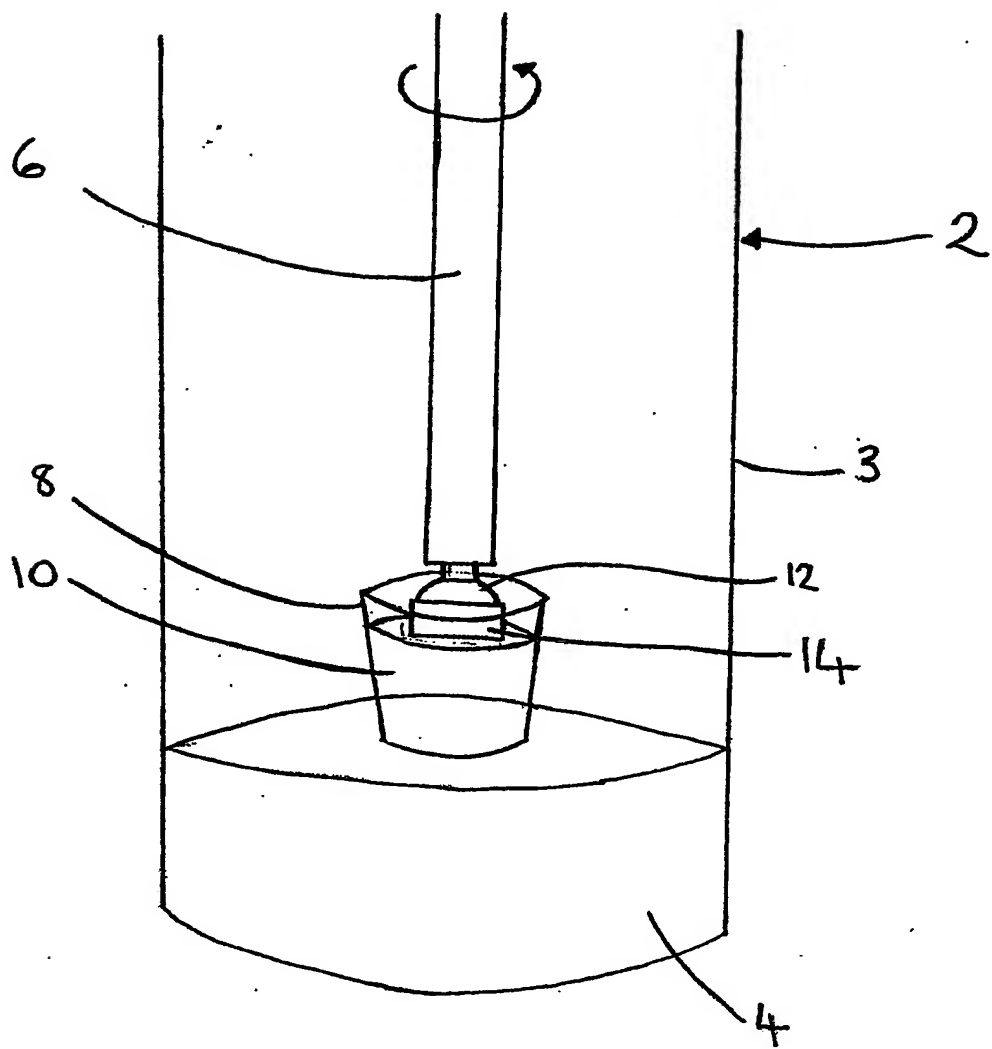


Fig 1

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